Tracing variability in the iodine isotopes and species along surface water transect from the North Sea to the Canary Islands

He, Peng; Aldahan, Ala; Hou, Xiaolin; Possnert, Göran

Published in:
Journal of Radioanalytical and Nuclear Chemistry

Link to article, DOI:
10.1007/s10967-015-4449-y

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

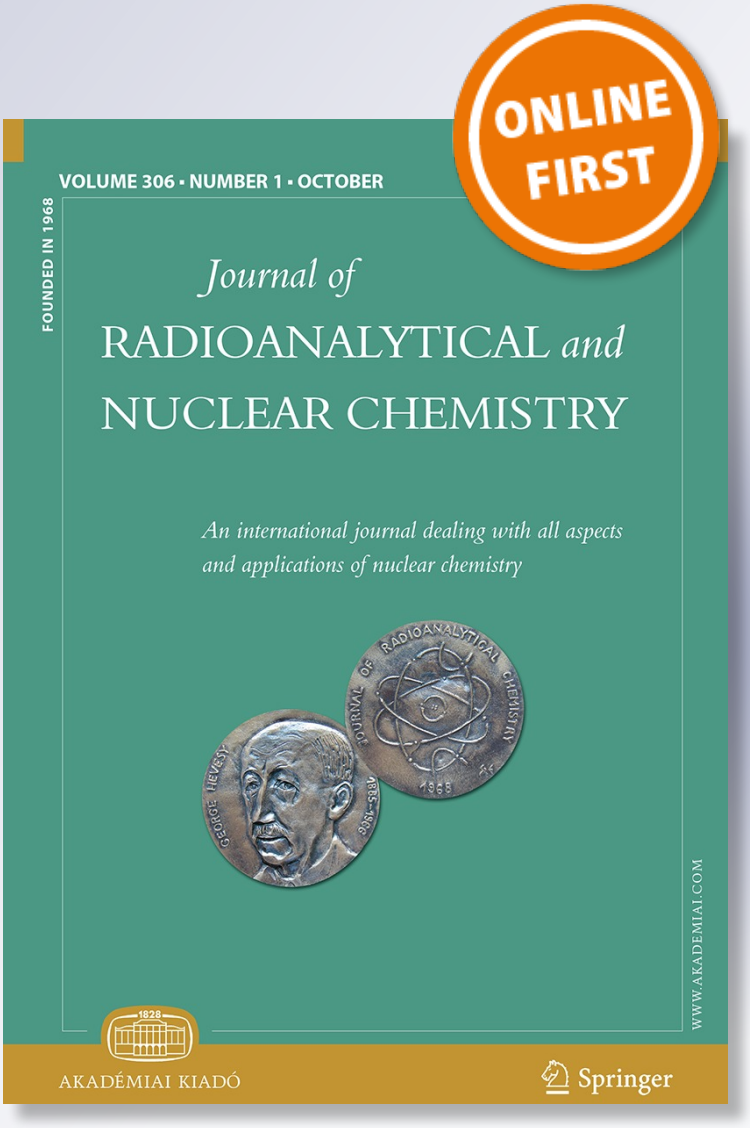
Tracing variability in the iodine isotopes and species along surface water transect from the North Sea to the Canary Islands

Peng He, Ala Aldahan, Xiaolin Hou & Göran Possnert

Journal of Radioanalytical and Nuclear Chemistry
An International Journal Dealing with All Aspects and Applications of Nuclear Chemistry

ISSN 0236-5731

J Radioanal Nucl Chem
DOI 10.1007/s10967-015-4449-y



Springer

J Radioanal Nucl Chem
DOI 10.1007/s10967-015-4449-y

Tracing variability in the iodine isotopes and species along surface water transect from the North Sea to the Canary Islands

Peng He[1] · Ala Aldahan[2,3] · Xiaolin Hou[4,5] · Göran Possnert[6]

Received: 31 March 2015

Abstract A complete transect of surface water samples from the North Sea to the Canary Islands was collected during a continuous period in 2010. The samples were analyzed for total ^{129}I and ^{127}I isotopes and their iodide and iodate species. The results indicate a large variability in the total ^{129}I and its species along the transect, whereas less change and variation are observed for the total ^{127}I and its species. Transport of ^{129}I from the western English Channel via Biscay Bay is the main source of ^{129}I in the northeastern Atlantic Ocean.

Keywords ^{129}I · Iodine species · Geochemical tracer · Atlantic Ocean

Introduction

The two major European nuclear reprocessing facilities, Sellafield (United Kingdom) and La Hague (France), have totally introduced more than 5500 kg radioactive ^{129}I into their surrounding marine environments [1, 2]. The anthropogenic plumes were subsequently transported to most northern hemisphere marine reservoirs through both oceanic and atmospheric pathways, eventually leading to 1–6 orders of magnitude increase of ^{129}I/^{127}I ratio in the seawater compared to the pre-anthropogenic natural value [3]. The major marine ^{129}I reservoirs are the English Channel, the North Sea, the Nordic Seas and the Arctic Ocean and even the northern parts of the North Atlantic [4–7]. However, the relatively high mobility and solubility of iodine in marine water suggest global scale transport through complex ocean currents and meteorological systems [8–10]. Therefore, in contrast to traditional investigated regions (i.e. Nordic Seas and the Baltic Sea), it becomes vital to broaden the study areas, particularly in the Atlantic Ocean that is south of the 60°N, in order to better monitor and investigate the environmental behavior of this radionuclide.

The major soluble species of iodine in seawater are iodate, iodide, and to a minor extent, organic iodine. Iodine is a redox sensitive element; iodide may sometimes appear as the dominant species in reducing environment aided by biological activities [11]. As an ideal oceanographic tracer, speciation analysis of ^{129}I provides a powerful tool for acquisition of information about sources and exchange of water masses in the ocean compared to using total ^{129}I alone. Furthermore, only few and scattered data exist on ^{129}I and its speciation in the marine environments south of the La Hague facility which make the region interesting for the understanding of applying the speciation approach for water mass identification. At the same time provides a comprehensive picture of environmental impact and radioactivity level.

We report here, the results of iodine isotopes and their species from the October 2010 surface water sampling

✉ Peng He
hphphp1985@163.com

1 Department of Earth Sciences, Chengdu University of Technology, Chengdu 610059, China

2 Department of Geology, United Arab Emirates University, Al Ain, UAE

3 Department of Earth Sciences, Uppsala University, 752 36 Uppsala, Sweden

4 Center for Nuclear Technology, Technical University of Denmark, Risø Campus, 4000 Roskilde, Denmark

5 Xi'an AMS Center, State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

6 Tandem Laboratory, Uppsala University, 751 20 Uppsala, Sweden

Published online: 10 September 2015

accomplished during the icebreaker *Oden* sailing from to Sweden to the Antarctica. This sampling program was a part of 2010/2011 Antarctica two-ship expedition, which was an international scientific cruise jointly funded by the Swedish Polar Research Secretariat and the US National Science Foundation (NSF). Part of the expedition was aimed at investigating iodine isotopes (^{129}I and ^{127}I) and species of iodine (I^- and IO_3^-) variability in surface water along transect from the North Sea through the English Channel and Northeastern Atlantic and some of the preliminary data have been published elsewhere [12–14]. The sampling transect covered the North Sea, the English Channel and the Northeastern Atlantic Ocean to the Canary Island (Fig. 1). Although part of the data were published earlier, the complete transect data are reported here for the first time.

Experimental

A total of 80 surface seawater samples with volumes of 0.5–2.0 L were collected during October–November 2010. These samples were immediately in situ filtered before sealed and stored in laboratory under dark and cold conditions. Anion-exchange chromatography was used to separate iodide and iodate from seawater. Each filtered samples spiked with 250 Bq $^{125}I^-$ tracer was loaded to the prepared anion exchange resin column (50–100 mesh, in NO_3^- form). After the seawater pass through, the column was washed with deionized water and 0.2 M $NaNO_3$ solution. The effluent was combined with the two washes for iodate extraction. The iodide fraction absorbed on column, however, was eluted with 60 ml of 5 % NaClO solution. 1 ml of solution was taken in each fraction for ^{127}I measurement using an X Series^{II} ICP-MS (Thermal Electron Corporation).

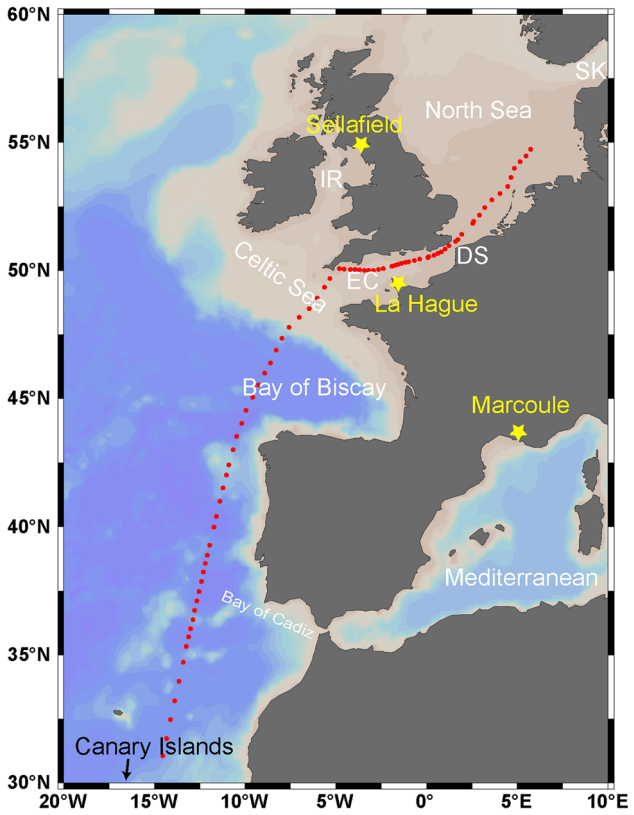


Fig. 1 Sampling locations of ^{129}I along the transect from the North Sea to the Canary Islands. Sampling sites are expressed as *red dots*. Three major European nuclear reprocessing facilities Sellafield, La Hague and Marcoule, are highlighted with *yellow stars*. *SK* Skagerrak; *IR* Irish Sea; *DS* Dover Strait; *EC* English Channel

Stable iodine (Woodward iodine, as a carrier) and chloroform was used for solvent extraction of iodine. Iodine was firstly reduced to iodide by adding 1.0 M $Na_2S_2O_5$ and 3.0 M HNO_3, then oxidized to I_2 using 1.0 M $NaNO_2$ and extracted into $CHCl_3$ phase, followed by $Na_2S_2O_5$ solution to be back-extracted into water. Iodine in the separated solution (as I^-) was precipitated as AgI and $^{129}I/^{127}I$ was then measured by AMS at the Tandem Laboratory, Uppsala University. ^{129}I standard NIST-SRM 4949C with an $^{129}I/^{127}I$ of 1.1×10^{-11} was used in AMS determination.

Chemical recoveries of iodine in fractions during the procedures, measured by ^{125}I, were all above 70 %. All chemical reagents used were of analytical grade and all solutions were prepared using deionized water (18.2 MΩ·cm^{-1}). The detection limit for ^{127}I calculated as 3 standard deviation of blank was 0.02 ppb and the total error is <3 % and the statistical error of the ^{129}I measurements was < 7 % at one standard deviation.

Results

Total ^{129}I and species

The sampling locations, as well as the corresponding analytical results are shown in Fig. 2. After around 50-fold increase in the North Sea, concentrations of ^{129}I along the transect exhibited a great drop, which decreased with more than four orders of magnitude afterwards, then leveled with some fluctuations from the Bay of Biscay to the Canary Islands. The average value of ^{129}I concentration for the entire transect was 7.28×10^{10} atoms/L, where the highest value of 4.67×10^{11} atoms/L appeared in the English Channel, while the lowest (4.3×10^7 atoms/L) occurred in the Northeastern Atlantic Ocean.

The ratios of iodide/iodate for ^{129}I were differed from that of total ^{129}I in the surface seawater samples. Relatively high values were observed in both the northern and southern parts of the transect. The highest values (>2.0)

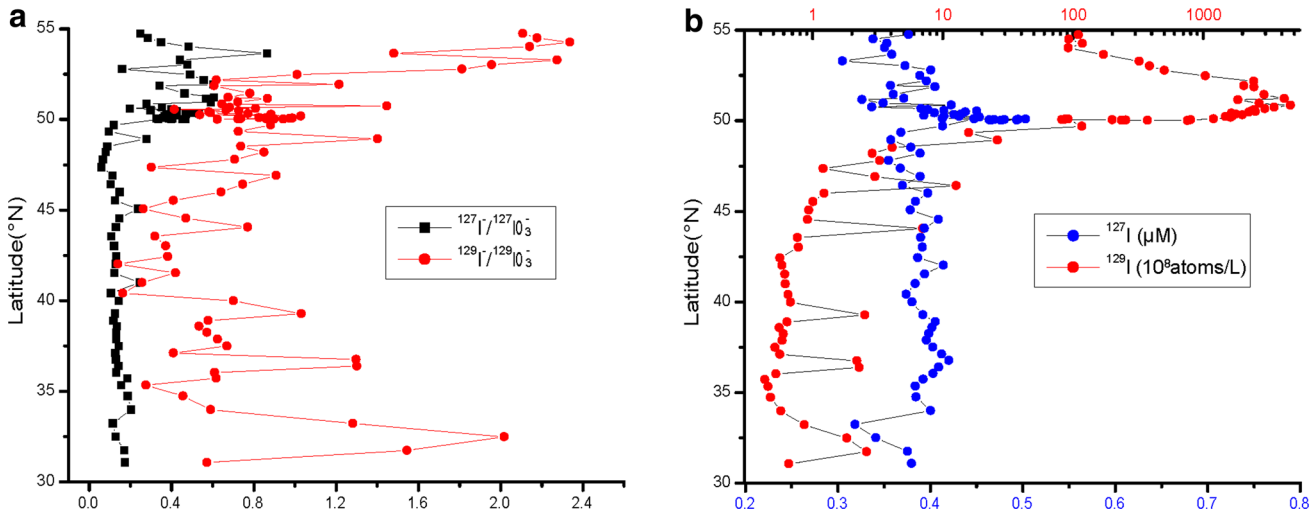


Fig. 2 Iodine isotopes and iodide/iodate in the surface seawater samples. **a** Iodide/iodate ratio for ^{127}I and ^{129}I and **b** concentrations of total ^{127}I and ^{129}I along the transect as a function of latitude

occurred in the shallow coastal regions of the North Sea. Peaks of high $^{129}I^-/^{129}IO_3^-$ values (>1.0) occur in the Northeastern Atlantic Ocean with the intensity increased south of 40°N. In the remaining samples the $^{129}I^-/^{129}IO_3^-$ values were, however, generally less than 1.0, suggesting iodate predominance in these seawaters. Considering the whole transect, the average $^{129}I^-/^{129}IO_3^-$ was 0.86 (<1.0).

Total ^{127}I and species

Distribution of total iodine and iodide/iodate for the ^{127}I isotope are given in Fig. 2. In general, ^{127}I and its species did not show wide variation compare to that of ^{129}I. The average concentrations for ^{127}I and $^{127}I^-/^{127}IO_3^-$ were 0.40 μM and 0.28, respectively. Total iodine slightly increased from the North Sea to the English Channel, where iodide/iodate remained around 0.42 in this region. In the Northeastern Atlantic Ocean, iodine and its species were generally leveled off with a few fluctuations. However, both of ^{127}I and $^{127}I^-/^{127}IO_3^-$ decreased and remained at relatively low levels.

Discussion

Distribution of ^{129}I and its species

The comprehensive picture of ^{129}I variations in the surface seawater going from the source region (i.e. the English Channel) into surrounding areas clearly indicates a pronounced change in both northward and southward directions. A 'Giant decline' in the concentration of ^{129}I occurs passing the Dover Strait to the open Atlantic Ocean, which reflects the northward major transport pathway of ^{129}I. However, the level of ^{129}I was still high in the southwest part of the English Channel with average concentration (4×10^{10} atoms/L) four times higher than that in the north part of the North Sea transect (1.0×10^{10} atoms/L; Fig. 3). In the Atlantic Ocean transect, particularly the northern part, the average concentration of ^{129}I was 3.4×10^8 atoms/L, corresponding to $^{129}I/^{127}I$ of 1.5×10^{-9} (Fig. 3). These values are comparable to that observed in the Denmark Strait Overflow Water (DSOW) in 2001 [15]. The observation suggests that transport of ^{129}I to southward direction of the English Channel cannot be ignored, and it can be an important source that eventually influences more southerly part of the Atlantic Ocean derived by the North Atlantic Gyre.

Our results of iodine species were consistent with those of other investigations that suggest iodide enrichment in shallow coastal and estuarine areas [16]. Average iodide/iodate value for ^{129}I in the North Sea was high (2.2), especially in the north part of the transect (Fig. 3). The reason for the high iodide/iodate for ^{129}I in the North Sea is proximity to the iodide-rich releases from La Hague. However, some of the samples were collected at >120 km distant from the coastline, thus it was difficult to distinguish the source of iodide, whether it was locally produced or transported from the inshore regions. The $^{129}I^-/^{129}IO_3^-$ values in the English Channel, the Celtic Sea and the Atlantic Ocean generally exhibited an iodate-dominant water, particularly in the middle part of Atlantic transect, where the average $^{129}I^-/^{129}IO_3^-$ was 0.34 (Fig. 3). This pattern may reflect the more oligotrophic environment in these areas compared to the North Sea, since organic activity is considered one of the major drives for iodate

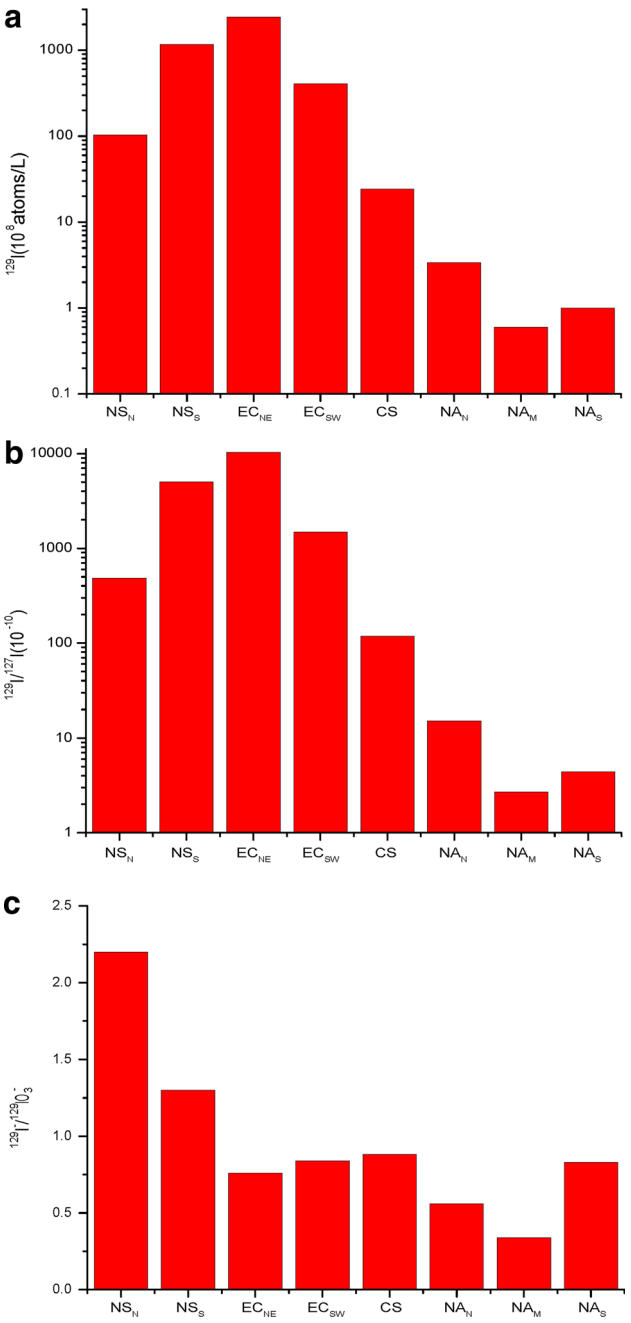


Fig. 3 Average values of **a** ^{129}I, **b** $^{129}I/^{127}I$ and **c** $^{129}I^{-}/^{129}IO_3^{-}$ in different parts of the transect from the North Sea to the Northeastern Atlantic Ocean. NS_N North Sea transect, northern part; NS_s North Sea transect, southern part; EC_{NE} English Channel transect, northeastern part; EC_{sw} English Channel transect, southwestern part; *CS* Celtic Sea; NA_N Northeastern Atlantic transect, northern part; NA_M Northeastern Atlantic transect, middle part; NA_S Northeastern Atlantic transect, southern part

reduction [17]. Besides, large discrepancy in the iodide/iodate between the ^{129}I and ^{127}I along the entire transect illustrates different sources for the two isotopes, as well as a slow redox rate transfer between iodide/iodate pair in the open sea environment.

Tracer applications

The distribution of anthropogenic ^{129}I was used to trace mixing and circulation of water masses in the marine environment. Our results and those of other investigations clearly indicate a northeastward transport of ^{129}I from the English Channel and the North Sea [6, 18]. Iodine-traced water masses in the English Channel west of the La Hague implied a high rate of water masses mixing westward as indicated by dramatic and consecutive decrease in the average ^{129}I concentrations from about 400×10^8, in the Channel, to 24×10^8 atoms/L in the Celtic Sea. Comparable average $^{129}I^{-}/^{129}IO_3^{-}$ values of these two adjacent areas ($\sim$0.85, Fig. 3) also confirm the La Hague derived ^{129}I as a predominant source in the Celtic Sea. However, one sample with relatively high $^{129}I^{-}/^{129}IO_3^{-}$ value (>1.2) may provide a clue of possible Sellafield derived ^{129}I in this region.

In general, ^{129}I and its iodide fraction were low in the whole Atlantic transect. However, the average $^{129}I^{-}/^{129}IO_3^{-}$ values were low between 40°N and 44°N and relatively high in the northern and southern parts. This feature is also coupled with occurrence of two ^{129}I and $^{129}I^{-}/^{129}IO_3^{-}$ peaks in the north and three of that in the south (Fig. 2). These high ^{129}I and their corresponding iodide suggest different sources from north and south. In the north part of the Atlantic section, La Hague is the major source, thus the high peaks of $^{129}I^{-}/^{129}IO_3^{-}$ represent ^{129}I speciation in the La Hague discharges after natural oxidation alternation. The peaks in the southern part of the transect, however, may attribute to influences of Mediterranean water parcels, which were likely carrying signals of the Marcoule facility releases. Thus, the occurrence of high ^{129}I and $^{129}I^{-}/^{129}IO_3^{-}$ values probably reflect specific circulation of Mediterranean Overflow Water (MOW) in the Atlantic Ocean [12]. If this suggested explanation is correct, then ^{129}I and its speciation can potentially be applied as sensitive tracers to label MOW in the intermediate layer of North Atlantic. Moreover, the high $^{129}I^{-}/^{129}IO_3^{-}$ levels of a Mediterranean origin may again confirm that the oxidation transformation of iodide to iodate is a rather slow process in the open ocean.

Environmental impact

The ^{129}I concentrations were 1–6 orders of magnitude above the estimated natural level ($\sim 4 \times 10^5$ atoms/L) and more importantly, higher than ^{129}I level in the ocean surface water after aboveground nuclear weapons testing ($\sim 1 \times 10^7$ atoms/L) [19]. This feature implied that contamination by anthropogenic ^{129}I has occurred through the whole transect of surface water analyzed here. The ^{129}I data reported here are also in agreement with ranges

Table 1 Reported ranges of ^{129}I, $^{129}I/^{127}I$ and $^{129}I^{-}/^{129}IO_3^{-}$ in different locations of ocean surface

Location	Sampling Year	$^{129}I(10^8$ atoms/L)	$^{129}I/^{127}I(10^{-10})$	$^{129}I^{-}/^{129}IO_3^{-}$	References
North Sea	2005	109–3603	435–17384	0.5–3.6	[20]
	2010	92–2450	436–10233	0.6–2.3	This work
English channel	1991	NG*	12.3–12.7	NG	[21]
	2005	26–3817	105–15827	0.5–0.9	[20]
	2010	82–4670	275–18771	0.4–1.4	This work
Celtic Sea	2005	32–47	NG	NG	[22]
	2010	3–117	12–470	0.7–1.4	This work
Western Atlantic Ocean					
Gulf of Mexico	1992	0.2	0.6	NG	[23]
Middle Atlantic Bight	1994	NG	1.1	NG	[24]
Labrador Sea	2001	1.3–4.5	NG	NG	[15]
Eastern Atlantic Ocean	2010	0.4–12	1.8–56	0.1–2.0	This work
Prior to nuclear era	Before 1940s	*0.004*	*0.015*	*NG*	[19]
Upground nuclear weapons testing	After 1940s	*0.1*	*0.5*	*NG*	[19]

For comparison, ^{129}I values of the pre- and post-nuclear era are also given in the table (in *Italic*)

* *NG* not given

reported by other investigations in the North Sea and the English Channel in 2005 [20]. However, levels of ^{129}I and its species in 2005 were relatively higher in the North Sea and lower in the English Channel than that collected in 2010 (Table 1). This may partly relate to sampling location where some of the 2005 sampling locations were more close to coastline, where biochemical processes were more efficient, as well as fewer samples were collected in the English Channel. Additionally, changes of ^{129}I marine discharges and ocean currents budget in the English Channel-North Sea region can also affect the ^{129}I distribution. For comparison, ^{129}I in seawater samples reported in the English Channel in 1995 were 1–3 orders of magnitude lower than the ones reported here, suggesting a fast and dramatic ^{129}I accumulation in the English Channel in the past 20 years [21].

In 2005, several seawater samples were collected in the Irish coast which indicated slightly higher ^{129}I concentration than the concentration reported here for the Celtic Sea [22]. This difference may reflect variable sources of ^{129}I in the Celtic Sea, where the north part was more influenced by the Irish Sea. Only few ^{129}I data are available in surface water of the western North Atlantic Ocean and they generally show lower concentration than the eastern Atlantic waters reported here for 2010 [15, 23, 24]. The source of the western North Atlantic ^{129}I is related to diluted Labrador Sea water mass (Table 1). However, the Labrador Sea water mass generally moves as intermediate and bottom water, the major part of the ^{129}I signal may not appear in the surface water along the western North Atlantic, but at depth.

Conclusions

This study showed clear anthropogenic ^{129}I signals in the surface water along a transect from the North Sea to the Canary Islands with a large decline in the concentration along the southward direction of the transect. The source of the ^{129}I is strongly related to the releases from the La Hague nuclear reprocessing facility as also imprinted in the iodine species distribution and iodine isotopic ratios in the investigated marine surface water. Despite anthropogenic ^{129}I values several orders of magnitude higher than the pre-anthropogenic natural level, it seems that at present there is no direct radioactivity hazard. However, it is worthwhile to monitor ^{129}I concentration, particularly in the English Channel water, considering the continuous discharge of ^{129}I from the nuclear reprocessing facilities.

Acknowledgments The authors thank the Swedish Polar Secretary and the Swedish Research Council For logistic and financial support. Thanks are also extended to the crew of the Icebreaker *Oden* for their continuous help and livelihood and to Anna Storm Sturevik for the generous help with the sampling onboard the ship. This work was also a project supported by Scientific Research Fund of Sichuan Provincial Education Department, China and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

References

1. Aldahan A, Alfimov V, Possnert G (2007) ^{129}I anthropogenic budget: major sources and sinks. Appl Geochem 22:606–618
2. Hou XL, Hansen V, Aldahan A, Possnert G, Lind OC, Lujaniene G (2009) A review on speciation of ^{129}I in the environmental and biological samples. Anal Chim Acta 632:181–196
3. He P, Aldahan A, Possnert G, Hou XL (2013) A summary of global ^{129}I in marine waters. Nucl Instr Meth B 294:537–541
4. Dahlgaard H, Herrmann J, Salomon J (1995) A tracer study of the transport of coastal water from the English Channel through the German Bight to the Kattegat. J Mar Syst 6:415–425
5. Kershaw PJ, McCubbin D, Leonard KS (1999) Continuing contamination of north Atlantic and Arctic waters by Sellafield radionuclides. Sci Total Environ 237:119–132
6. Alfimov V, Aldahan A, Possnert G, Winsor P (2004) Anthropogenic ^{129}I in seawater along a transect from the Norwegian coastal current to the North Pole. Mar Pollut Bull 49:1097–1104
7. Dahlgaard H (1995) Transfer of European coastal pollution to the arctic: radioactive tracers. Mar Pollut Bull 31:3–7
8. Smith JN, Ellis KM, Kilius LR (1998) ^{129}I and ^{137}Cs tracer measurements in the Arctic Ocean. Deep Sea Res Part I 45:959–984
9. Reithmeier H, Lazarev V, Rühm W, Nolte E (2010) Anthropogenic ^{129}I in the atmosphere: overview over major sources, transport processes and deposition pattern. Sci Total Environ 408:5052–5064
10. Moran J, Oktay S, Santschi P, Schink D (1999) Atmospheric dispersal of ^{129}I from nuclear fuel reprocessing facilities. Environ Sci Technol 33:2536–2542
11. Wong GTF, Cheng XH (2008) Dissolved inorganic and organic iodine in the Chesapeake Bay and adjacent Atlantic waters: speciation changes through an estuarine system. Mar Chem 111:221–232
12. He P, Hou XL, Aldahan A, Possnert G, Yi P (2013) Iodine isotopes species fingerprinting environmental conditions in surface water along the northeastern Atlantic Ocean. Sci Rep 3:2685
13. He P, Hou XL, Aldahan A, Possnert G (2013) Radioactive ^{129}I in surface water of the Celtic Sea. J Radioanal Nucl Chem 299:249–253
14. He P, Aldahan A, Possnert G, Hou XL (2013) Temporal variation of iodine isotopes in the North Sea. Environ Sci Technol 48:1419–1425
15. Smith JN, Jones E, Moran S, Smethie WM Jr, Kieser W (2005) Iodine 129/CFC 11 transit times for Denmark Strait overflow water in the Labrador and Irminger seas. J Geophys Res 110:C05006
16. Wong GTF, Cheng XH (1998) Dissolved organic iodine in marine waters: determination, occurrence and analytical implications. Mar Chem 59:271–281
17. Wong GTF (1995) Dissolved iodine across the Gulf Stream Front and in the South Atlantic Bight. Deep Sea Res Part I 42:2005–2023
18. Alfimov V, Aldahan A, Possnert G, Kekli A, Meili M (2004) Concentrations of ^{129}I along a transect from the North Atlantic to the Baltic Sea. Nucl Instr Meth B 223:446–450
19. Snyder G, Aldahan A, Possnert G (2010) Global distribution and long-term fate of anthropogenic ^{129}I in marine and surface water reservoirs. Geochem Geophys Geosyst 11:Q04010
20. Hou XL, Aldahan A, Nielsen S, Possnert G, Nies H, Hedfors J (2007) Speciation of ^{129}I and ^{127}I in seawater and implications for sources and transport pathways in the north sea. Environ Sci Technol 41:5993–5999
21. Raisbeck G, Yiou F, Zhou Z, Kilius L (1995) ^{129}I from nuclear fuel reprocessing facilities at Sellafield (UK) and La Hague (France); potential as an oceanographie tracer. J Mar Syst 6:561–570
22. Keogh S, Aldahan A, Possnert G, Finegan P, Leon Vintro L, Mitchell P (2007) J Environ Radioact 95:23–38
23. Schink D, Santschi P, Corapcioglu O, Sharma P, Fehn U (1995) ^{129}I in Gulf of Mexico waters. Earth Planet Sci Lett 135:131–138
24. Santschi P, Schink D, Corapcioglu O, Oktay-Marshall S, Fehn U, Sharma P (1996) Evidence for elevated levels of ^{129}I in the deep Western Boundary Current in the Middle Atlantic Bight. Deep Sea Res Part I 43:259–265